REPORT SM-49105-~~M8~~ Q8

STRESS CORROSION CRACKING OF TITANIUM ALLOYS AT AMBIENT TEMPERATURE IN AQUEOUS SOLUTIONS

PROGRESS REPORT FOR PERIOD
OCTOBER, NOVEMBER AND DECEMBER 1968
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MCDONNELL DOUGLAS ASTRONAUTICS COMPANY

MCDONNELL DOUGLAS
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Quarterly Progress Report
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Prepared by:

Theron L Mackay

T. L. Mackay, Ph.D.
Senior Research Scientist

D. R. Mash

D. R. Mash, Ph.D.
Head, Materials Department

ASTROPOWER LABORATORY
McDonnell Douglas Astronautics Company
Western Division
Newport Beach, California

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ABSTRACT

Aging of beta forged Ti-8Al-1Mo-1V in the temperature range 900°F to 1100°F reduced fracture toughness and increased susceptibility to stress corrosion cracking. Selected area diffraction of beta forged Ti-8Al-1Mo-1V showed a face-centered tetragonal for martensitic alpha phase and coplanar slip was shown to be associated with $\{1\bar{1}\bar{1}\}$ planes. Aging of martensitic structure reduces the amount of retained beta. The reduction in fracture toughness of aged alpha-beta alloys appears to be highly dependent on the microstructure of the beta phase in aged heat treat condition. Specimens of the titanium alloys, Ti-8Al-1Mo-1V, Ti-4Al-1Mo-1V and Ti-4Al-1.5Mo and 0.5V were irradiated with thermal neutrons. A technique for observing Mo^{99} distribution in titanium alloys was developed employing NTB-3 nuclear track emulsion.

The effect of a stress field on the distribution of tritium in beta forged Ti-8Al-1Mo-1V at 600°F was determined. An increasing concentration of tritium at the alpha-beta interface with increasing stress field was observed.

1.0 INTRODUCTION AND SUMMARY

Several investigations have been conducted to determine the particular factors that make a titanium alloy susceptible to SCC in a specific environment. The factors suggested have included coplanar arrays of dislocations, ordering, rupture of passive films, chemisorption of ions, formation of hydrides and segregation of interstitial or substitutional solute atoms to dislocations. In general, it is recognized that for an alloy to be susceptible to transgranular stress corrosion cracking, it must develop wide slip steps when plastically deformed, rupture of a passive surface film and be exposed to an environment in which slip step is not partially repassivated within a critical time period.

The Astropower Laboratory is engaged in a program of NASA sponsored research to develop fundamental knowledge about the mechanism of SCC of titanium alloys in aqueous saline solutions at ambient temperature. Study of the behavior of alpha type and alpha beta type alloys is emphasized because they are known to exhibit susceptibility to SCC and are candidate materials for tankage and supersonic applications. The results obtained for October, November and December 1968 are presented in this report.

2.0 EXPERIMENTAL EVALUATIONS

2.1 Effect of Microstructure on Susceptibility to Stress Corrosion Cracking of Beta Forged Ti-8Al-1Mo-1V

It had been shown previously[1] that beta forged Ti-8Al-1Mo-1V was immune to SCC. Aging at 1100°F decreased the fracture toughness and increased susceptibility to SCC. In this report period, the stress corrosion behavior of beta-forged Ti-8Al-1Mo-1V, aged at 900°F for 75 hours, was investigated in 3% NaCl solution at ambient temperature. Stress corrosion tests were conducted by loading single-edge notched specimens.

The initial stress intensity factor, K_{Ii}, to propagate a crack in 3% NaCl salt solution for as-forged and aged Ti-8Al-1Mo-1V is shown in Table I. Aging of the beta forged Ti-8Al-1Mo-1V in the temperature range 900°F to 1100°F reduces the fracture toughness and susceptibility to stress corrosion cracking in aqueous salt solutions at ambient temperature.

2.2 Transmission Electron Microscopy

It was shown previously[1] that retained beta in as-forged Ti-8Al-1Mo-1V restricted planar dislocation arrays in the acicular martensitic alpha phase; slip occurred simultaneously across several lamellae of retained beta and acicular martensitic alpha grains. Blackburn[2] showed that two forms of martensitic alpha occur in Ti-8Al-1Mo-1V: (1) a face centered tetragonal martensitic α' which is formed from the range 1600°F to 1700°F and (2) a hexagonal martensite α'' which is formed above 1700°F. Selected area diffraction patterns of beta-forged Ti-8Al-1Mo-1V showed only the face-centered tetragonal martensitic, α', which was quite surprising since this alloy was forged above the beta transus. From these results it appears that the crystal structure obtained from quenching above the beta transus of alpha-beta alloys is related to the rate of quenching since the large beta-forged compressor disc was quenched at a much slower rate than the thin sheet material employed by Blackburn. The coplanar slip planes in the martenistic alpha phase, α', of beta forged Ti-8Al-1Mo-1V was identified as $\{1\bar{1}\bar{1}\}$.

A tensile specimen of beta-forged Ti-8Al-1Mo-1V, aged at 1100°F, 8 hours, W.Q., was strained 5% and observed by transmission

TABLE I

STRESS INTENSITY FACTOR FOR BETA-FORGED AND AGED BETA-FORGED Ti-8Al-1Mo-1V IN AIR AND 3% NaCl SOLUTION

Heat Treatment	K_{IC} ksi $\sqrt{in}$	K_{Ii} ksi $\sqrt{in}$	Time to Fracture (mn)	$\frac{K_{Ii}}{K_{IC}}$
As forged	78.3			
		82.5	—	
		90.0	—	
		82.5	—	
1100°F, 8 hrs., AQ	58.0			
		37.0	6	.64
		37.0	5	
900°F, 75 hrs., AQ	56.7			
		28.6	4	
		26.8	5	
		26.0	8	.46

electron microscopy. Figure 1 shows acicular alpha + beta structure in an unstrained region. The growth of the alpha phase across β lamellae is shown in this micrograph.

Coplanar slip was observed in the alpha phase (see Figure 2) of beta-forged Ti-8Al-1Mo-1V aged at 1100°F. Slip occurred simultaneously across several martensitic alpha and retained beta lamellae of similar orientation. Aging of beta forged Ti-8Al-1Mo-1V at 1100°F reduced volume percent and distribution of beta phase, and this appears to be responsible for the reduction of the fracture toughness and susceptibility to stress corrosion cracking.

A tensile specimen of Ti-6Al-4V was water quenched from above the beta transus 1850°F and strained approximately 10%. No evidence of copolanar dislocation arrays or slip planes could be observed in the acicular martensitic alpha phase for this heat treatment. (See Figure 3.) Stress appears to be relieved by cross slip within the martensitic alpha grains.

2.3 Distribution of Beta Stabilizer, Mo, in Alpha-Beta Titanium Alloys

It has been proposed that high chemical reactivities at slip planes is due to segregation of solute atoms to dislocations.[3] It has been suggested that solute atoms make monatomic jumps into sites at the core of a slowly moving dislocation.[4] As this effect would enrich slip plane with solute atoms, subsequent shear on the same plane must produce a chemical discontinuity at the alloy surface.

A study has been initiated to measure the concentration of Mo in the alpha and beta phases of alpha-beta alloys. For this study, three alloys were selected; Ti-8Al-1Mo-1V, Ti-4Al-3Mo-1V, and Ti-4Al-1.5Mo-0.5V. Ti-8Al-1Mo-1V and Ti-4Al-3Mo-1V are commercial alloys. Ti-4Al-1.5Mo-0.5V is an experimental alloy obtained from Battelle Memorial Institute. A chemical analysis of the three alloys showed 1.33 w/oMo, 2.96w/oMo and 1.53w/oMo for beta-forged Ti-8Al-1Mo-1V, Ti-4Al-1Mo-1V, and Ti-4Al-1.5Mo-0.5V respectively. Table II shows the alloys and their heat treatments used in this investigation. The microstructure has been previously reported.

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Figure 1. Transmission Electron Micrograph of Beta Forged Ti-8Al-1Mo-1V, Aged at 1100°F, 8 hours, W.Q. Note Beta, Arrows 1.

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Figure 2. Transmission Electron Micrograph of Beta Forged Ti-8Al-1Mo-1V, Aged at 1100°F, 8 hours, W.Q. Strained Approximately 5%. Note Shearing of Beta Lamellae, Arrows 1.

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Figure 3. Transmission Electron Micrograph of Acicular Martensitic Ti-6Al-4V (1850°F, W.Q.) Strained Approximately 10%. Note Retained Beta.

TABLE II

TITANIUM ALLOYS IRRADIATED WITH THERMAL NEUTRONS

Alloy	Heat Treatment
Ti-8Al-1Mo-1V	duplex annealed
Ti-8Al-1Mo-1V	duplex annealed + 1600°F 2 hrs, WQ
Ti-8Al-1Mo-1V	beta forged
Ti-8Al-1Mo-1V	beta forged + 900°F, 20 hrs AC
Ti-4Al-3Mo-1V	as received
Ti-4Al-3Mo-1V	1600°F, 2 hrs, WQ
Ti-4Al-3Mo-1V	1600°F, 2 hrs, WQ + 900°F, 20 hrs, AC
Ti-4Al-1.5Mo-.5V	as received
Ti-4Al-1.5Mo-.5V	1600°F, 2 hrs, WQ
Ti-4Al-1.5Mo-0.5V	1600°F, 2 hrs, WQ + 900°F, 20 hrs, AC

Specimens 1/2" x 1/2" were irradiated for one hour in the Northrup Triga reactor with a thermal neutron flux of 10^{13} n/cm^2. The nuclear reaction $Mo^{98}(n)Mo^{99}$ produced by a thermal neutron induces the beta emitter reaction product Mo^{99} with a half life of 66 hours. Specimens of pure Mo were also irradiated to serve as a standard.

The determination of the distribution of molybdenum in alpha and beta phases by electron microautoradiography employing a monolayer of Kodak NTE nuclear track emulsion was shown previously[1] to be inconclusive due to the poor efficiency of the thin emulsion films used to detect the energetic beta particles from Mo^{99}. Kodak NTB-3 and NTB-2 emulsions were investigated in this experiment. A uniform emulsion layer was best obtained by dipping a glass rod in the emulsion and subsequently drawing the rod across the surface of the mounted specimen. A dilution of 5 parts water to 1 part emulsion was required to produce an emulsion film thin enough to examine in the electron microscope. It was found necessary to apply emulsion in total darkness.

A decay period of seventeen days elapsed before a successful technique was developed for detecting emitted beta particles from Mo^{99}. An emulsion of NTB-3 was exposed for eight hours on a specimen of irradiated pure Mo; an electron microautoradiograph is shown in Figure 4. A thin emulsion layer of NTB-3 was applied to specimens of the titanium alloy Ti-4Al-3Mo-1V which had been solution heat treated at 1600°F, 2 hours, W.Q. Another specimen was solution heat-treated at 1600°F, 2 hours, W.Q. plus aging at 900°F, 20 hours, A.C. Both were exposed for a period of 67 hours. Figures 5 and 6 are electron microautoradiographs of Ti-4Al-3Mo-1V of the two heat treatments, respectively. The solution heat treatment at 1600°F showed a rather uniform distribution of Mo in the beta phase. The specimen which was solution annealed at 1600°F and aged at 900°F showed a higher concentration of Mo at alpha beta interface than within the beta grains.

2.4 Effect of Stress on Hydrogen Microsegregation and Embrittlement

The presence of large amounts of hydrogen in alpha and alpha-beta alloys is known to cause embrittlement. In certain areas, the concentration has been observed at high residual stresses locations. Yet there is

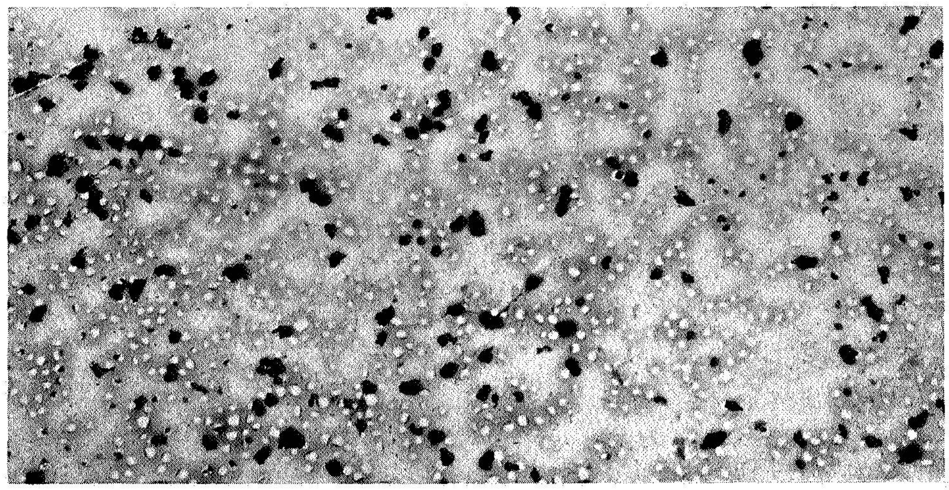

Figure 4. Electron Microautoradiograph of Mo^{99} in Pure Mo. Magnification: 2500 x

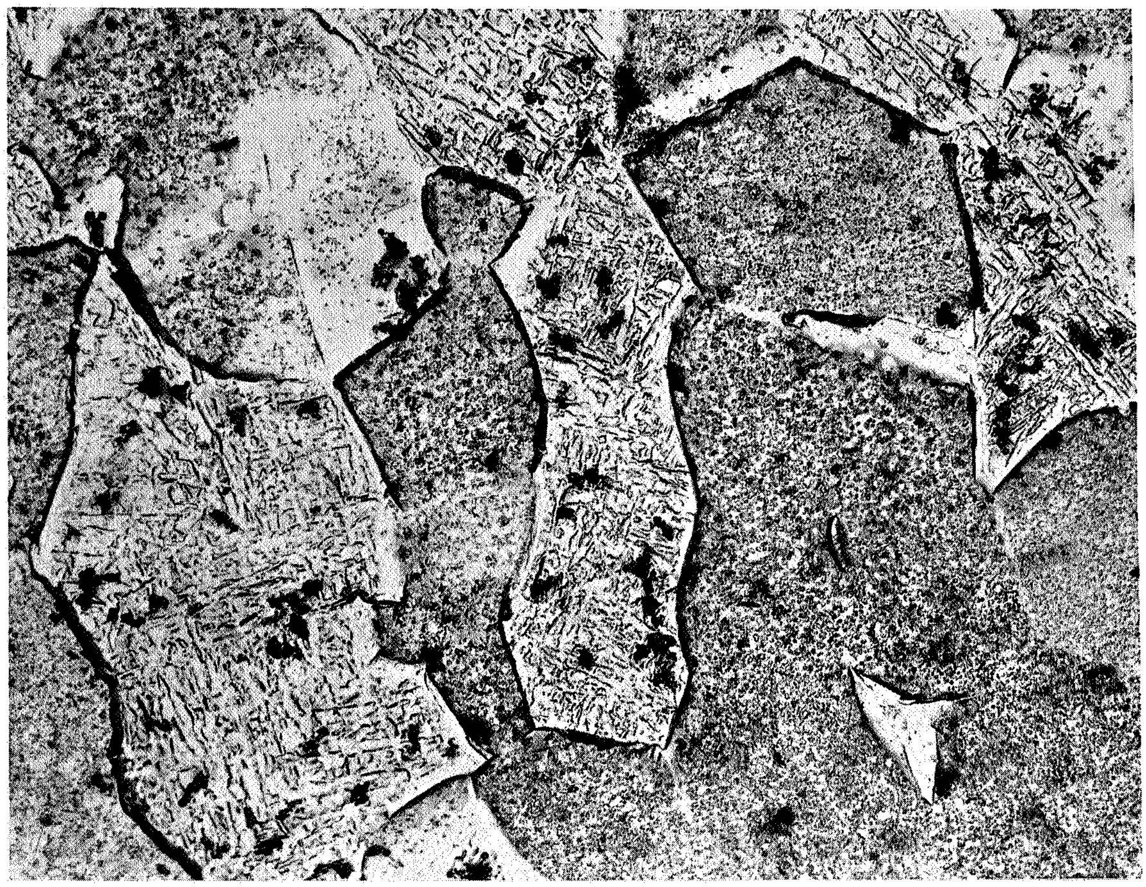

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Figure 5. Electron Microautoradiograph of Mo^{99} in Ti-4Al-3Mo-1V Solution Annealed at 1600°F, 2 hours, W.Q. Magnification: 3000x

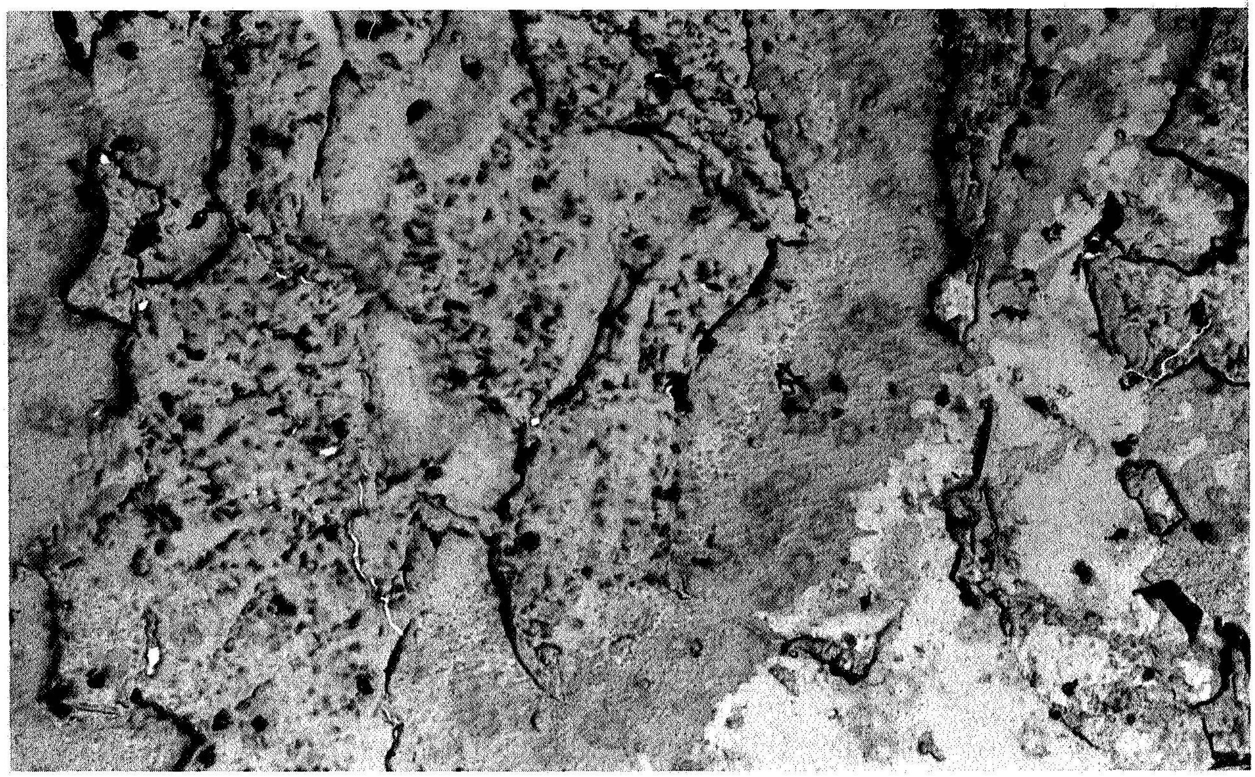

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Figure 6. Electron Microautoradiograph of Mo^{99} in Ti-4Al-3Mo-1V Solution Annealed at 1600°F, 2 hours, W. Q. and Aged at 900°F, 20 hours, A. C.

no experimental data on the effect of a stress field on the diffusion and equilibrium distribution of hydrogen in titanium alloys at more elevated temperatures, 500-600°F. Where hot salt cracking is a problem, it has been shown that hydrogen diffusion along grain boundaries does indeed occur and cause stress corrosion cracking.

Experiments have been initiated to determine the diffusion and equilibrium distribution of hydrogen (tritium) under a varying stress field in high purity titanium and Ti-8Al-1Mo-1V at 600°F.

High purity iodide titanium rod 99.95% was obtained and beta forged Ti-8Al-1Mo-1V was used in these experiments. The tensile properties at 600°F of pure Ti and Ti-8Al-1Mo-1V containing 300 ppm were reported previously.[1]

To measure the effect of a stress field on the hydrogen distribution, a 1/4 inch rod with tapered gauge to 0.100 inch at center was employed. A specimen of Ti-8Al-1Mo-1V weighing 4.36 gm was charged with 275 ppm of tritium. The specimen was held at 80% of yield strength (0.2% offset Y.S.) for 200 hours. The specimen was machined flat through the center line and the hydrogen distribution was determined by electron microradiography using a monolayer of Kodak NTE emulsion. An exposure time of 90 minutes was used for this analysis. Figure 7 shows the tritium distribution at the center of the tapered rod where the stress was 80% of Y.S. At this stress level an extremely high concentration of tritium was observed in the beta phase and at alpha-beta grain boundaries. Figures 8 and 9 show electron microautoradiographs of tritium at 65% and 54% of Y.S. At these stress levels the tritium is highly concentrated in the alpha-beta grain boundary regions. At a low stress level, 12.5% of Y.S., only the normal high concentration in beta phase is observed (see Figure 10).

To measure the effect of a stress field on the hydrogen distribution in pure titanium, a 1/2 inch rod with tapered gauge to 0.100 inch at center was charged with 476 ppm and held at 80% of Y.S. at 600°F for 200 hours. The specimen was machined flat through the center line and a monolayer of Kodak NTE was exposed for 40 minutes. The distribution will be measured during the next report period.

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Figure 7. Electron Microautoradiograph of Ti-8Al-1Mo-1V Containing 275 ppm Tritium at 67, 500 psi Stress at 600°F. Magnification: 12, 000 x

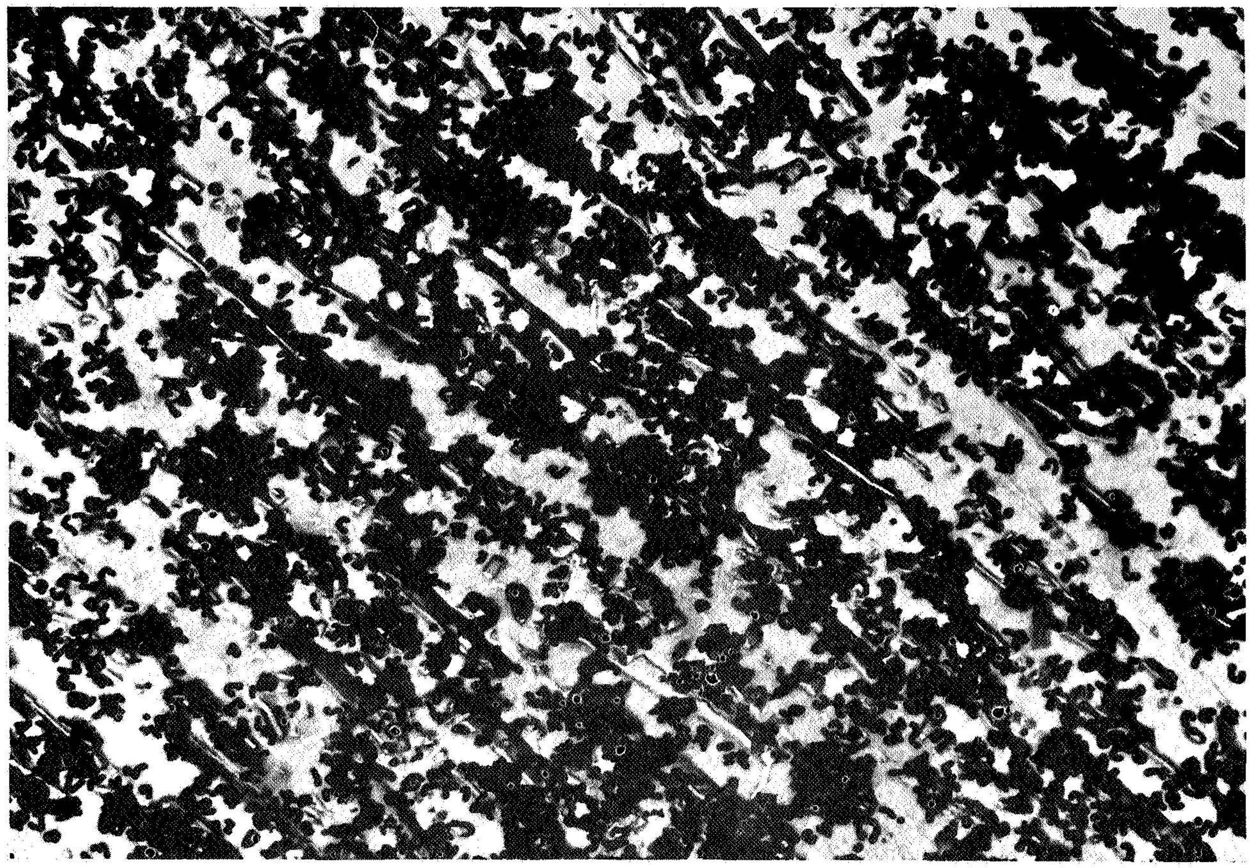

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Figure 8. Electron Microautoradiograph of Ti-8Al-1Mo-1V Containing 275 ppm Tritium at 54, 500 psi Stress at 600°F. Magnification: 12, 000 x

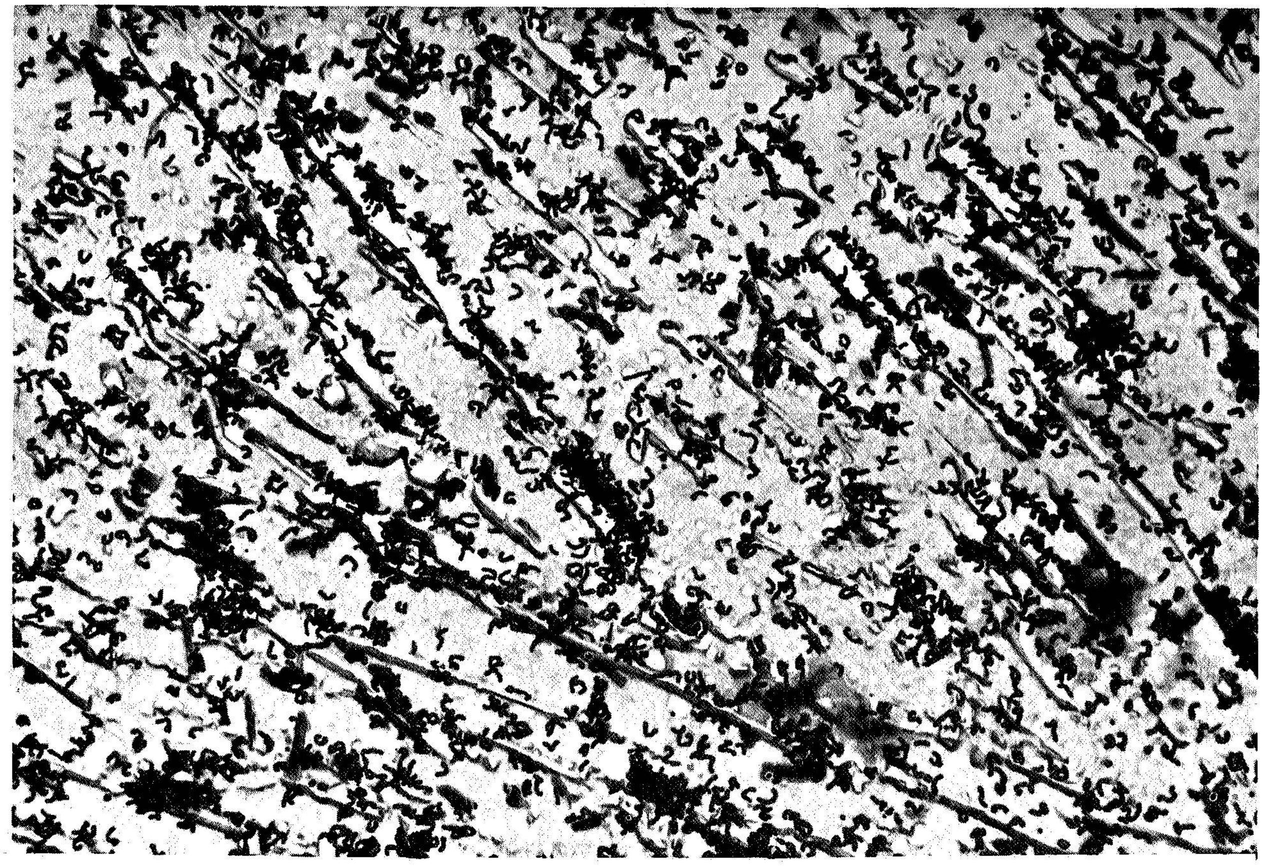

Figure 9. Electron Microautoradiograph of Ti-8Al-1Mo-1V Containing 275 ppm Tritium at 45,500 psi Stress at 600°F. Magnification: 12,000x

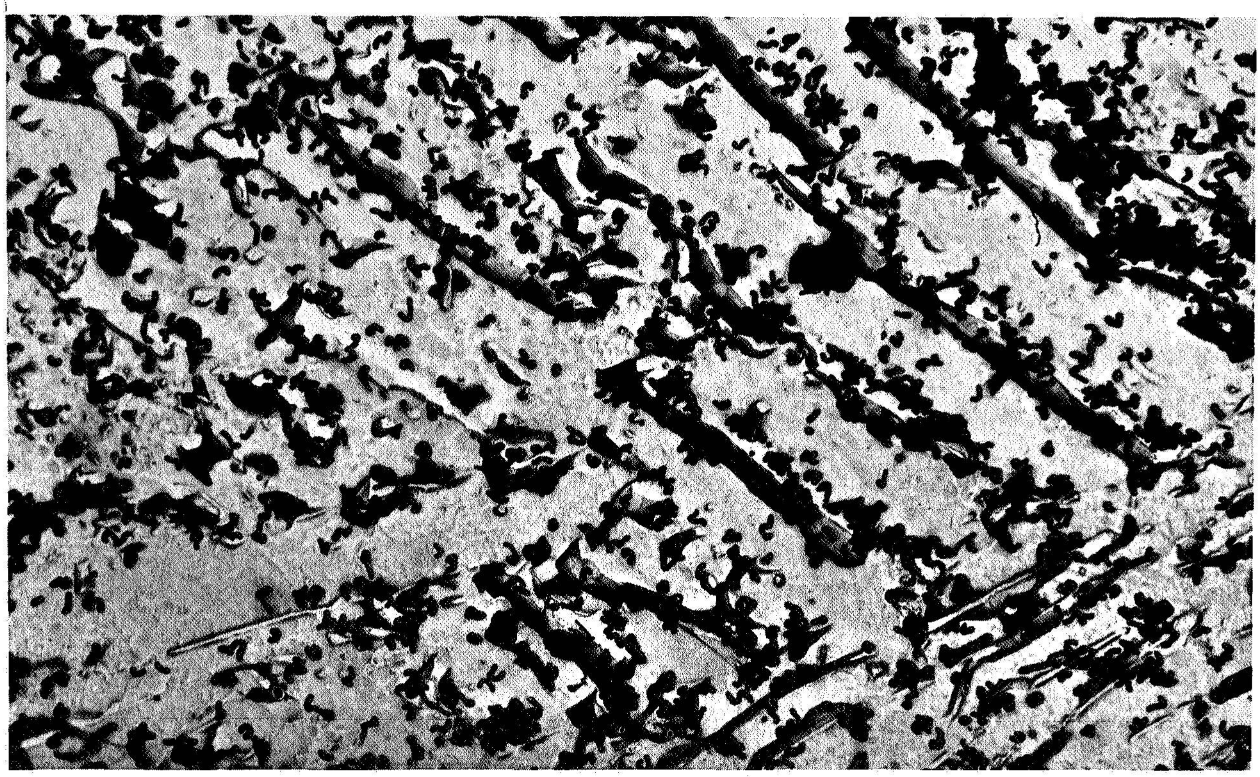

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Figure 10. Electron Microautoradiograph of Ti-8Al-1Mo-1V Containing 275 ppm Tritium at 10,500 psi Stress at 600°F. Magnification: 12,000x

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